



Stop Using Conventional Methods in AAS

Fast and Reliable Analysis in Petrochemistry using Microwave Digestion and Solid AA[®]

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The analysis of trace metals is an integral part of petrochemical process and product control. Process performance considerations as well as environmentally-related legislation require certain elements to be analysed in crude oil, intermediate and final products. Different elements can cause corrosion, destroy catalysts or have other negative influences on process equipment and its performance (e.g. nickel, vanadium, chromium), while others are toxic, and thus must not be contained in petroleum-based fuels (e.g. lead, arsenic, mercury). Multiple analytical methods are in use for this purpose, with their respective methods of sample preparation.

Atomic spectrometry is commonly used for trace element analysis, mostly ICP OES and AAS. Both methods can only handle liquid samples of low viscosity, so crude oil and heavy to medium fractions have to be dissolved in a suitable solvent or mineralised prior to the analysis, only light fractions can be analysed directly.

Sample preparation for spectroscopic analysis

Different methods of sample preparation are available for petroleum samples, including acid digestion, wet or dry ashing and dissolution in solvents. The stability of organic solutions is rather poor, so that samples and standards cannot be stored – in some cases solutions are only stable for few hours due to adsorption loss on container surfaces [1]. Stability is not an issue for aqueous solutions, thus mineralisation methods should be preferred over organic solutions. If samples contain particulate matter, mineralisation is the only method for the reliable determination of total element contents, since particles would be lost by sedimentation in a solution.

Among the mineralisation methods, the ashing methods have certain disadvantages, mainly because open vessels are used for these procedures. This can lead to contamination from the lab atmosphere, but more important, involves the risk of losing volatile elements. While elements like mercury and lead are known to be potentially volatile, even metals considered to be thermally stable, like nickel and vanadium, can form organic complexes that are volatile at ashing temperatures [2]. Both the loss of volatile species and the contamination of the sample are largely precluded when using sealed pressure vessels.

This is evidenced in table 1 where the recovery rates for mercury, as the most volatile metal, in certified reference materials or spiked real samples are compared by various digestion methods. Both open methods obviously lead to significant analyte losses. Only in the pressure vessel can the samples be digested without significant losses.

Microwave-heated pressure digestion also allows a precise reaction control through power output controlled by temperature and pressure. Oil samples can contain very reactive components that

can already react exothermically at a low temperature. To keep such reactions under control a precise monitoring of the individual digestion vessels is useful to adjust the heating output in accordance with the progression of the reaction. The digestion duration is also reduced significantly compared to open methods.



Figure 1: TOPwave[®] is a versatile microwave digestion system offering a variety of digestion vessels, fulfilling all requirements of modern applications.

	ASTM D 5863-00a (muffle furnace) WFR [%]	Open wet ashing (heating plate) WFR [%]	Microwave pressure digestion WFR [%]
Kerosene (approx. 10 mg/kg)	2,0	-	98
Paraffin-base oil (approx. 10 mg/kg)	2,2	-	91
Refined oil 20 cSt (approx. 10 mg/kg)	2,1	-	99
Conostan standard (100 mg/kg)	-	54	-
Naphtha 1	-	-	88
Naphtha 2	-	-	91
Naphtha 3	-	-	92
Heavy oil 1	-	-	94
Heavy oil 2	-	-	98

Table 1: Recovery rate (WFR) for mercury using different digestion methods

Step	1	2	3
Temperature [°C]	130	160	230
Max. pressure [bar]	80	80	100
Max. output [%]	70	70	100
Heat ramp [min]	10	10	10
Hold time [min]	10	10	30

Table 2: Temperature program for microwave digestion

Samples were digested in the microwave system TOPwave[®] (Fig. 1), equipped with the high performance vessels CX 100 (100 mL, max. 300 °C, max. 100 bar). For this a mixture of 6 mL nitric acid, 2 mL hydrochloric acid and 2 mL hydrogen peroxide was used together with the temperature program shown in table 2. The program contains two steps at low temperature to digest reactive sample components. The stable components are then mineralised at high temperature. The sample weight was 100–200 mg in each case.

Microwave-assisted acid digestion obviously is the most reliable procedure for petroleum sample preparation, avoiding analyte loss and mineralising samples in a short time with high throughput.

Analysis

Samples are analysed by spectrometric methods after mineralisation. From the analytical point of view, Graphite Furnace AAS (GF AAS) has some advantages over Flame AAS and ICP OES. The latter depend on the nebulisation of samples, which is very sensitive towards changes in sample viscosity. This makes it particularly difficult to obtain reliable results if sample and standard compositions vary, thus special calibration or matrix correction techniques have to be applied. The sensitivity of these techniques is often not sufficient for the concentration ranges to be detected after sample preparation [3]. In addition to that, the high carbon content of organic solutions requires special adaptations (e.g. auxiliary oxidant) in flame and plasma based instruments. These factors usually have no influence on GF AAS because the whole sample volume is injected directly, and the organic matrix can easily be removed during sample pyrolysis. The influence of the matrix on the measurement signal is thus lower. Therefore calibration with aqueous standards is often feasible even for pure organic samples, simplifying the analytical procedure. An additional benefit of GF AAS is its high sensitivity, allowing low element concentrations to be analysed. For these reasons, GF AAS is a popular technique for this kind of applications [3, 4, 5].

A rather new approach to oil analysis is the direct introduction of crude oil and similar samples into the graphite furnace by means of a special autosampler. This option has been commercially available for more than a decade with the introduction of solid AA® systems by Analytik Jena. The

solid AA® technique uses the SSA 600 autosampler (Fig. 2) to carry solid samples on a graphite platform directly into the graphite furnace. Crude oil is not exactly a solid sample, but due to its high viscosity it can be considered more solid than liquid in terms of handling and sampling, and solid AA® is the perfect tool for its analysis.

This unique technology can speed up the analytical process significantly, as it reduces sample preparation to an absolute minimum. Oil samples simply have to be homogenised as usual. Then a small amount (typically 0.5–2.5 mg) is placed directly onto the sample carrier. The manual work ends at this point: Samples are automatically weighed to the nearest 1 µg on the integrated microbalance and then carried into the graphite furnace for measurement. The large sample tray allows fully automatic analysis of up to 84 samples without any intervention by the user.

After the measurement sample carriers can immediately be reused for the next sample.



Figure 2: The autosampler SSA 600 carries solid samples on a graphite platform directly into the graphite furnace.

Besides drastically reducing the time consumption and the manual work of sample preparation, solid AA® brings additional benefits: Errors that might occur during sample preparation, like dilution errors, contamination or analyte loss by adsorption or volatile species, cannot happen because the original sample is analysed without any pretreatment. Without being diluted during sample preparation, lower concentrations can be analysed using solid AA® compared to



Figure 3: The contrAA® atomic absorption spectrometers are the first and only commercially available instruments for HR-CS AAS.

conventional methods. Analytik Jena GF AAS instruments allow adjustment of the sensitivity according to sample concentrations. Thus a wide range of concentrations from lowest µg/kg up to the percent range can be analysed easily.

A wide range of elements, including As, Cd, Pb, Fe, Cr, Ni and V, have been analysed in crude oil and related matrices by solid AA® in research and industry. Investigations have shown that direct analysis of crude oil is equally accurate as conventional spectroscopic methods [6, 7], and that its detection limits and sensitivity are superior to conventional spectroscopic methods and comparable or superior to mass spectrometric methods [3, 8].

Apart from the usual single-element determinations in GF AAS, applications have been developed that are impossible using conventional methods. The direct and simultaneous determination of Cr and Fe in crude oil is one of these applications [9]. This is only possible using solid AA® in combination with High-Resolution Continuum Source AAS (HR-CS AAS, Fig. 3), which allows multiple absorption lines to be evaluated simultaneously thanks to its capability of displaying the sample absorption spectrum – a feature unique in AAS.

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